

The Kondo effect and the single-atom transistor

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Transistors

Arguably, the most important invention of the past century, the transistor is often cited as the exemplar of how scientific research can lead to useful commercial products. The discovery of the transistor has clearly had enormous impact, both intellectually and commercially, upon our lives and work. A major vein in the corpus of condensed matter physics, quite literally, owes its existence to this breakthrough. It also led to the micro-miniaturization of electronics, which has permitted us to have powerful computers on our desktops that communicate easily with each other via the internet. The resulting globalization of science, technology and culture is now transforming the ways we think and interact.

Over the past 30 years, silicon technology has been dominated by Moore's law: the density of transistors on a silicon integrated circuit doubles about every 18 months. The same technology that allows us to shrink the sizes of devices has allowed us to learn new physics. The synergy of technological development and new physics has been remarkably successful in the past few years, and it is difficult to anticipate the many new directions that synergy will take in the next decade or so.

To continue the increasing levels of integration beyond the limits mentioned above, new approaches and architectures are required. In today's digital integrated circuit architectures, transistors serve as current switches to charge and discharge capacitors to the required logic voltage levels. It is also possible to encode logic states by the positions of individual electrons (in quantum dot single-electron transistors, for example) rather than by voltages. Such structures are scalable to molecular levels, and the performance of the device improves as the size decreases. Artificially structured single-electron transistors studied to date operate only at low temperature, but molecular or atomic sized single-electron transistors could function at room temperature.

Before we turn to the single-atom transistors, the subject of this article, we need to learn about the Kondo effect.

The Kondo effect

This is a physical phenomenon that was discovered in the 1930s, explained in the 1960s and has been the subject of numerous reviews since the 1970s. Although the Kondo effect is a well-known and widely studied phenomenon in condensed matter physics, it continues to capture the imagination of both experimentalists and theorists. The effect arises from the interactions between a single-magnetic atom, such as cobalt, and the many electrons in an otherwise non-magnetic metal such as copper. Such an impurity typically has an intrinsic angular momentum or spin that interacts with all the surrounding electrons in the metal. As a result, the mathematical description of the system is a difficult many-body problem.

The electrical resistance of a pure metal usually drops as its temperature is lowered, because electrons can travel through a metallic crystal more easily when the vibrations of the atoms are small. However, the resistance saturates as the temperature is lowered below about 10 K due to the presence of crystal lattice defects in the material, such as vacancies, interstitials, dislocations and grain boundaries. Electrical resistance is related to the amount of backscattering from defects, which hinders the motion of the electrons through the crystal. This textbook resistive behaviour of a metal changes dramatically when magnetic atoms, such as cobalt, are added. The electrical resistance increases as the temperature is lowered further, in contrast to that of a pure metal. This effect was

first observed in the 1930s. The effect is illustrated in Figure 1.

This behaviour does not involve any phase transition, such as a metal-insulator transition. A parameter called the Kondo temperature (roughly speaking the temperature at which the resistance starts to increase again) completely determines the low-temperature electronic properties of the material. There have been many observations of an anomalous increase in the resistance of metals at low temperature. Yet it took until 1964 for a satisfactory explanation to be proposed. Theorists can calculate the probability with which an electron will be scattered when the defect is small. However, for larger defects the calculation can only be performed using perturbation theory – an iterative process in which the answer is usually written as a series of smaller and smaller terms. In 1964, Kondo made a startling discovery when considering the scattering from a magnetic ion that interacts with the spins of the conducting electrons. He found that the second term in the calculation could be much larger than the first. The result is that the resistance of a metal increases logarithmically when the temperature is lowered. Hence the name 'Kondo effect'. The behaviour of the resistance of a metal and a 'quantum dot' are remarkably different, as shown in Figure 1. The reasons for this will be discussed in a later section.

Kondo's theory correctly describes the increase in resistance at low temperatures. However, it also makes the unphysical prediction that the resistance will be infinite at even lower tempera-

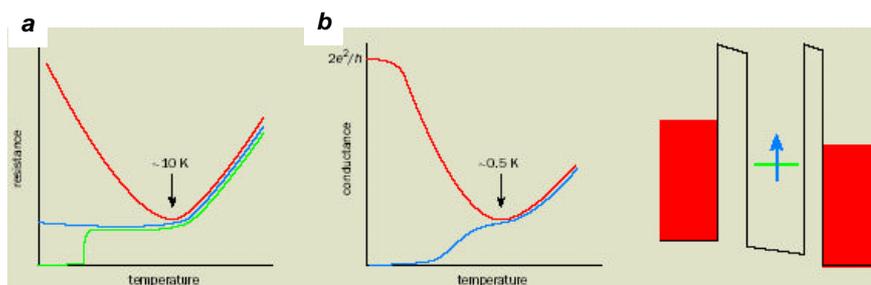


Figure 1. Kondo effect in (a) a metal, and (b) a quantum dot. See text for discussion. (Right) Illustration of magnetic impurity.

tures. It turns out that Kondo's result is correct only above a certain temperature, which became known as the Kondo temperature, T_K . As mentioned earlier, the Kondo effect only arises when the defects are magnetic – in other words, when the total spin of all the electrons in the impurity atom is non-zero. These electrons coexist with the mobile electrons in the host metal, which behave like a sea that fills the entire sample. In such a Fermi sea, all the states with energies below the so-called Fermi level are occupied, while the higher-energy states are empty.

In 1961, Anderson proposed the simplest model for a magnetic impurity in a metal. In this model, the impurity has only one electron with energy E . In this case, the electron can quantum-mechanically tunnel from the impurity and escape, if E is greater than the Fermi level of the metal. Otherwise it remains trapped. In this picture, the defect has a spin of $1/2$ and its z -component is fixed as either 'spin up' or 'spin down'. However, the so-called exchange processes can take place that effectively flip the spin of the impurity from spin up to spin down or vice versa, while simultaneously creating a spin excitation in the Fermi sea. Figure 2 illustrates what happens when an electron is taken from the magnetic impurity and put into an unoccupied energy state at the surface of the Fermi sea. The energy needed for this process is large, between 1 and 10 eV for magnetic impurities. Classically, it is forbidden to take an electron from the defect without putting energy into the system. In quantum mechanics, however, the Heisenberg uncertainty principle allows such a configuration to exist for a very short time – around $\hbar/|E|$, where \hbar is the Planck constant. Within this time scale, another electron must tunnel from the Fermi sea back to the impurity. However, since the uncertainty principle says nothing about the spin of this electron, its z -component may point in the opposite direction. In other words, the initial and final states of the impurity can have different spins. This spin exchange qualitatively changes the energy spectrum of the system (Figure 2c). When many such processes are taken together, one finds that a new state – known as the *Kondo resonance* – is generated with exactly the same energy as the Fermi level.

Such a resonance is effective at scattering electrons with energies close to

the Fermi level. Since the same electrons are responsible for the low-temperature conductivity of a metal, the strong scattering from this state increases the resistance. The Kondo resonance is unusual. Energy eigenstates usually correspond to waves for which an integer number of half wavelengths fits precisely inside a quantum box, or around the orbital of an atom. In contrast, the Kondo state is generated by exchange processes between a localized electron and free-electron states. Since many electrons need to be involved, the Kondo effect is a many-body phenomenon. It is important to note that the Kondo state is always 'on resonance' since it is fixed to the Fermi energy. Even though the system may start with an energy E that is very far away from the Fermi energy, the Kondo effect alters the energy of the system so that it is always on resonance. The only requirement for the effect to occur is that the metal is cooled to sufficiently low temperatures below the Kondo temperature T_K .

Enter nanotechnology

Nanotechnology aims to manipulate materials at the atomic scale. An important tool in the field is the scanning tunnelling microscope (STM), which can image a surface with atomic resolution, move individual atoms across a surface and measure the energy spectrum at particular locations. Recently, the STM has been used to image and manipulate magnetic impurities on the surface of metals, opening a new avenue of research into the Kondo effect. Previously, physicists could only infer the role of the Kondo effect from measurements of

resistance and magnetic susceptibility. With the advent of the STM, however, physicists can now simply 'photograph' the surface and thereby resolve the position of the atoms prior to studying the phenomenon. Scanning tunnel microscopy has moved the Kondo effect in the direction of imaging and manipulation. What the STM cannot do – at least not yet – is alter the properties of the magnetic impurity and its coupling to the metal. However, this is precisely the direction in which physicists studying quantum-dot devices are moving. Quantum dots are small structures that behave like artificial atoms. Some quantum dot devices are illustrated in Figure 3.

Quantum dots are often called artificial atoms since their electronic properties resemble those of real atoms. A voltage applied to one of the gate electrodes of the device controls the number of electrons, N , that are confined in the dot (Figure 3). If an odd number of electrons is trapped within the dot, the total spin of the dot, S , is necessarily non-zero and has a minimum value of $S = 1/2$. This localized spin, embedded between large electron seas in the two leads, mimics the cobalt-in-copper system. And many of the known Kondo phenomena can be expected to occur in these transistor-type devices.

Scanning tunnel microscopy and quantum-dot devices have provided new tools for studying the Kondo effect with unprecedented control. Some of the recent studies have counterparts in conventional metal-magnetic impurity systems, and some are unique to artificial nanostructures.

One of the main distinctions between a quantum dot and a real metal is related to

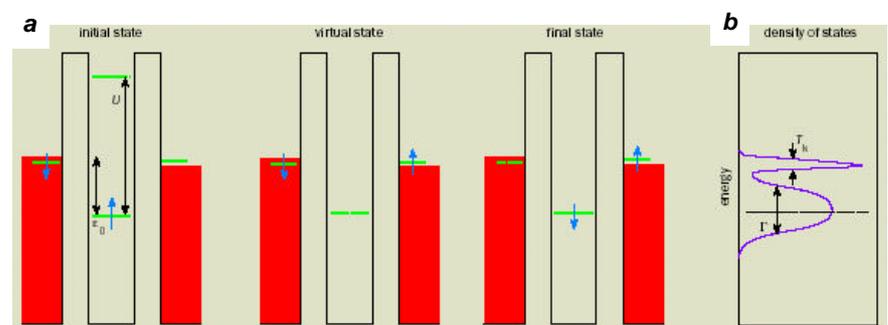


Figure 2. *a*, Anderson model for a magnetic impurity. Successive panels show the quantum mechanical tunnelling of the electron on the impurity to the surrounding Fermi sea in the metal, and the impurity state occupied by an electron from the Fermi sea in the metal; *b*, Kondo resonance near the Fermi energy. See text for discussion.

their different geometries. In a metal, the electron states are plane waves, and scattering from impurities in the metal mixes electron waves with different momenta. This momentum transfer increases the resistance. In a quantum dot, however, all the electrons have to travel through the device, as there is no electrical path around it. In this case, the Kondo resonance makes it easier for states belonging to the two opposite electrodes to mix. This mixing increases the conductance (i.e. decreases the resistance). In other words, the Kondo effect produces the opposite behaviour in a quantum dot to that of a bulk metal, as shown in Figure 1. The advantage of quantum dots is the ease with which the parameters of these artificial atoms can be controlled. External 'knobs' allow the discrete energy-level structure of the device to be varied, as well as the number of electrons trapped within the dot.

Like the resistance of a bulk sample in the Kondo regime, the conductance of a quantum dot depends only on T/T_K . With quantum dots, this universality can be readily checked, because the parameters that define T_K can be easily changed with the turn of a knob. The Kondo effect disappears when the number of electrons on the quantum dot is even. In contrast, when there is an odd number of electrons, the Kondo effect produces the opposite behaviour, i.e. the conductance increases at low temperatures. Moreover, at the lowest temperatures, the conductance approaches the quantum limit of conductance $2e^2/h$, where e is the charge of an electron.

Investigations into the Kondo effect are far from complete. One ongoing debate concerns the so-called Kondo cloud. The many electrons that are involved in the spin-flip processes in Figure 2 combine to build the Kondo resonance. The Kondo cloud consists of electrons that have previously interacted with the same magnetic impurity. Since each of these electrons contains information about the same impurity, they effectively have information about each other. In other words, the electrons are mutually correlated. The Holy Grail for research on the Kondo effect is to know whether it is possible to measure and control the Kondo cloud. But perhaps an equally important quest is to understand the time evolution of such a many-body quantum state. For example, how does the state build up? Is it possible to suddenly switch on the

exchange interaction in a quantum-dot experiment? Would such experiments allow us to measure how the accompanying Kondo cloud forms? The Kondo cloud also provides a possible mechanism to investigate the interactions between magnetic impurities. For example, how do the two many-body states that are formed around two separated localized magnetic moments merge?

Single-atom transistor using the Kondo effect

Precisely the revival that was spoken of in the earlier paragraphs has now taken place. Two papers published in *Nature* 13 June, report transistor action in a

single-atom, making use of the Kondo effect!

The smallest quantum dot that one can imagine would be a single-atom. This has recently been achieved! Jiwoong Park, Abhay N. Pasupathy, Jonas I. Goldsmith, Connie Chang, Yuval Yaish, Jason R. Petta, Marie Rinkoski, James P. Sethna, Hector D. Abruna, Paul L. McEuen and Daniel C. Ralph working at Cornell University and the University of California at Berkeley based their transistor on a single-cobalt atom suspended in an organic compound (Park, *J. et al.*, *Nature*, 2002, **417**, 722–725). Trapping a molecule (which holds a magnetic atom) between two metal electrodes to make such a transistor, is a formidable task. The molecule needs suitable chemistry

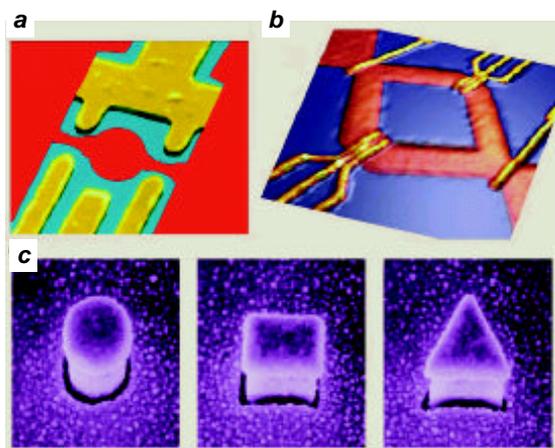


Figure 3. A quantum dot can be defined by applying voltages to the surrounding gate electrodes. *a*, Changing the voltages on the lower-left and lower-right gates controls the tunnelling between the dot and the external electrodes; *b*, Dots in an interferometer device; *c*, Dots of different shapes yield different values of impurity spin.

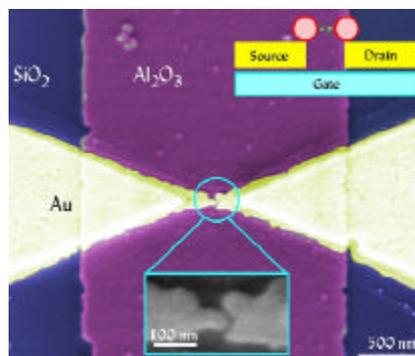


Figure 4. Configuration used to achieve the single-atom transistor. Gold electrodes form the source and drain. Electromigration is used to etch them down to 1 nm size. The complex molecule that binds to gold is shown schematically by large circles. Within this molecule is the single cobalt atom (used in the Cornell experiments) or the divanadium molecule (used in the Harvard experiments). The tiny bridge between the gold electrodes is shown enlarged.

that will bind it to the two electrodes, bridging the gap between them. This binding needs to be strong enough to withstand the measurements. The electrodes can be at most 1 nm apart. Conventional patterning techniques cannot attain this size. The two groups used unconventional 'electron beam lithography' to achieve a 10 nm wire. They deposited a gold wire about 10 nm thick onto a silicon substrate and then coated it with the complex molecule. The team then made a gap in the wire about 1 nm wide by using *electromigration*, so that the exposed tips formed source and drain electrodes (Figure 4). Electromigration is the movement of atoms in a material when a current flows through it. It is a nuisance in electronic chips and circuits. However, clever experimentalists can exploit even such nuisances to their advantage. In this instance, the property of electromigration of thinning down materials and breaking thin wires, has been used to create a tiny gap between two gold electrodes.

Molecules of the organic complex then slipped into this gap, taking a cobalt atom with them. A layer of silicon dioxide insulated the gap region from the silicon substrate, which acted as the gate electrode. In a similar manner, Wenjie Liang, Matthew P. Shores, Marc Bockrath, Jeffrey R. Long and Hongkun Park working at Harvard University and the University of California at Berkeley trapped divanadium molecules between gold electrodes – also 1 nm apart – and used aluminium oxide to isolate the gap region from their silicon gate electrode (Liang, W. *et al*, *Nature*, 2002, **417**, 725–729). Such entrapment of the molecule is often an occasional lucky event. There is no viable technique to ensure successful trapping. However, the presence of a single-molecule can be established from its conduction properties.

Both teams then measured the current flowing from the source to the drain as

they varied the voltage between these electrodes for a range of gate voltages. For each device, the researchers found that the current flowed only at certain gate voltages, which were related to the energy that an electron needs to hop on, or off, the bridging atom or molecule. This behaviour is the hallmark of a single-electron transistor, but both groups also found that more electrons took part in the current flow when they placed their devices in a magnetic field. This phenomenon clearly arises from the Kondo effect in which a single-magnetic entity – such as a cobalt atom or a divanadium molecule – interacts with the electrons in the non-magnetic material around it. As we have seen earlier, the Kondo effect reduces the resistance of quantum dots. In this case the single-atom forms the quantum dot. The experiments actually measured the differential conductance (dI/dV) from the current-voltage characteristics.

The repulsive Coulomb interaction prevents the addition of an extra electron to the molecule. This extra energy to add an electron can be reduced to zero using a gate electrode. At a certain gate voltage, an electron can hop on from the source to the molecule, but the addition of another electron is prevented by the Coulomb repulsion. The first electron must move to the drain before the second electron can hop on. This 'one by one' electron motion is the hallmark of single-electron tunnelling. In these experiments, the molecule is tuned between two states that differ by one charge and one spin unit. In one state the mechanism is single-electron tunnelling. In the next state with an odd number of electrons on the molecule, transport is mediated by the Kondo effect for quantum dots, which has been discussed in the previous section. This remarkable behaviour is observed in both experiments.

Both teams also found that the exact electronic properties of their transistors

could be tuned by changing the chemical make-up of the organic compounds. This determines the quality of the electrical connection between the atom or molecule and the electrodes. Both groups are now investigating these effects in transistors based on other atoms and molecules.

The future

The motion of electrons in such a transistor has been described as a complex dance by one of the authors (McEuen). Switching action is one property of a transistor that has been demonstrated. Bardeen, Brattain and Shockley were concerned about the 'amplification properties' of the transistors they had invented. It remains to be seen whether amplification can be achieved, to any experimentally observable extent, in such single-atom transistors. The behaviour of the Kondo cloud also remains to be understood. Needless to say, both groups are probably busy working on these aspects, even as you read this.

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